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Di- and Tri(tertiary phosphine) Complexes of Palladium(I)

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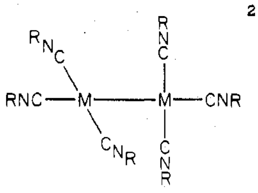
Addition of diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 2–4) or *cis*-$Ph_2PCH{=}CHPPh_2$ to $[Pd_2(CNCH_3)_6][PF_6]_2$ yields yellow crystalline complexes $[Pd_2(diphosphine)_2(CNCH_3)_2][PF_6]_2$. These have been characterized by ^{31}P and ^{1}H NMR spectroscopy, infrared spectroscopy, and solution electrical conductivities. These data indicate that the ions have symmetrical unbridged structures with each diphosphine chelating a single palladium ion. Addition of the triphosphine $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$ to $[Pd_2(CNCH_3)_6][PF_6]_2$ produces crystalline $[Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2][PF_6]_2$. The ^{31}P spectrum of the cation indicates that there are three distinct phosphorus environments in it. A bridged structure in which each triphosphine ligand chelates a single palladium ion and also acts as a bridge to coordinate the second palladium is proposed for this species. None of these new Pd(I) dimeric complexes show any tendency to insert carbon monoxide or methyl isocyanide into the Pd–Pd bond. Attempts to synthesize Pd(I) complexes from the reaction of $(PhCN)_2PdCl_2$, $Pd_2(dibenzylideneacetone)_3$, and $Ph_2P(CH_2)_nPPh_2$ (n = 2–4) yielded mixtures in which $(diphosphine)PdCl_2$ was the principal product. The arsine ligand in $Pd_2(Ph_2AsCH_2AsPh_2)_2Cl_2$ is readily substituted by $Ph_2PCH_2PPh_2$ to yield $Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$ with only trace amounts of the mixed species $Pd_2(Ph_2PCH_2PPh_2)(Ph_2AsCH_2AsPh_2)Cl_2$ forming during reaction. Addition of $Ph_2PCH_2CH_2PPh_2$ to $Pd_2(Ph_2AsCH_2AsPh_2)_2Cl_2$ produces $Ph_2P(CH_2)_2PPh_2PdCl_2$ in chloroform solution and $(Ph_2P(CH_2)_2PPh_2)_2Pd$ in benzene solution.

Introduction

Dinuclear palladium(I) compounds (and their platinum congeners) with six two-electron donor ligands display several unusual characteristics. The geometry of these species involves planar coordination about each of the two metal ions which are directly connected via a metal–metal bond. Structural studies in the solid state indicate that the dihedral angle between the two planes is variable. For the dinuclear isocyanide complexes $(RNC)_6M_2^{2+}$, X-ray crystallographic investigation of $(CH_3NC)_6Pd^{2+}$ (**1**)[1,2] indicates that these two planes are perpendicular. With bridging diphosphine ligands acting to constrain the orientation of the coordination planes in compounds of the type $M_2(Ph_2PCH_2PPh_2)XY$ (M = Pd, X = Y = Br;[3] M = Pd, X = Cl, Y = $SnCl_3$,[4] M = Pt, X = Y = Cl[5]), the dihedral angle between these planes lies in the narrow range of 42–38°. Bridging groups with greater restrictions can force the two coordination planes into coplanarity as found in **4**[6] and **5**.[7]



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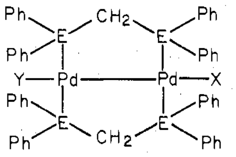
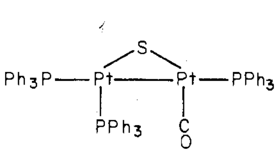


2, E = P
3, E = As



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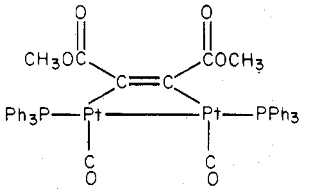

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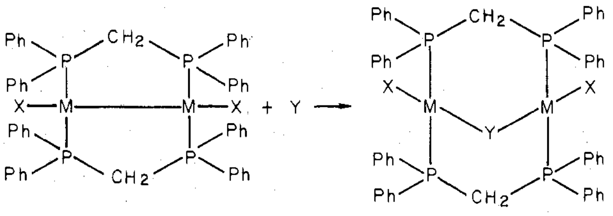
Palladium dimers of type **1** are fluxional while at comparable temperatures their platinum analogues are rigid.[1,8,9] Rapid axial–equatorial exchange of the isocyanide ligands has been observed by ^{1}H NMR spectroscopy. The intraionic process responsible for this interchange appears to involve a transient distortion of the palladium coordination into a tetrahedral geometry wherein all three isocyanide ligands on a particular palladium become equivalent. During this process, exchange of isocyanide ligands between the two metals does not occur.

Dimers of palladium and platinum of type **2** exhibit unusually reactive metal–metal bonds. These dimers undergo the facile insertion of small molecules via eq 1.[10–17] As a consequence of this reaction the two metal atoms move apart by about 0.5 Å. In some cases these insertions are reversible. The fact that both metal ions are coordinatively unsaturated undoubtedly assists in promoting these insertions, but unsaturation is not sufficient to confer such reactivity. Although complexes of type **1** are also unsaturated, they are largely unreactive toward the substrates Y of reaction 1.



(1)

Y = CO, CNR, SO_2, S, N_2R^+, CH_2, RC≡CR

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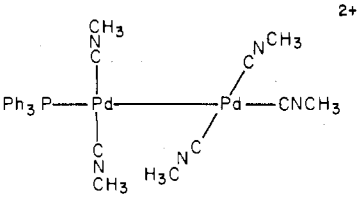
This study has been concerned with producing palladium(I) dimers by using potentially bridging di- and triphosphine ligands. Three points are of interest. (1) How would polyphosphine ligands orient themselves about the two metal centers? A bidentate phosphine could chelate a single metal or could behave as a bridging ligand by attaching itself to the two metal atoms. At present there is little evidence available that would enable predictions to be made about these geometric preferences. (2) Would phosphine ligands other than bis(diphenylphosphino)methane support the insertion of small molecules into the Pd–Pd bond and stabilize the A-frame geometry of the product? (3) Would the polyphosphine complexes display fluxional behavior?

Three routes to the synthesis of palladium(I) complexes have been employed in this work. The first involves the use of the conproportionation reaction of a Pd(II) complex, $(PhCN)_2PdCl_2$, a Pd(0) complex, tris(dibenzylidineacetone)dipalladium, and a diphosphine. In the case of bis(diphenylphosphino)methane, we have shown that this reaction offers a convenient and reliable route to the preparation of **2**.[11] The second route involves substitution of the relatively labile arsine ligands in $Pd_2(Ph_2AsCH_2AsPh_2)_2Cl_2$ (**3**),[11] the arsine analogue of **2**. The final approach involves substitution reactions of $[Pd_2(CNCH_3)_6][PF_6]_2$. Earlier studies in this laboratory have shown that triphenylphosphine substitution of **1** occurs stepwise to give exclusively the axially substituted species **6** and **7**.[8] In contrast addition of bis(diphenylphosphino)methane results in both substitution and isocyanide insertion into the Pd–Pd bond so that **8** is formed.[10,11]



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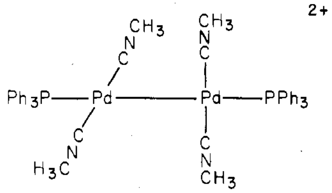

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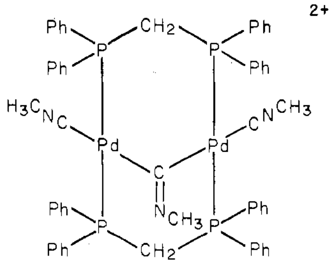

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Experimental Section

Preparation of Compounds. $Pd_2(Ph_2ECH_2EPh_2)_2Cl_2$[11] (E = P, As) and $[Pd_2(CNCH_3)_6][PF_6]_2$[8] were prepared as described previously. The phosphine ligands were purchased from Strem Chemicals. Complexes of the type (diphosphine)$PdCl_2$ were prepared from $(PhCN)_2PdCl_2$ by the method of Steffen and Palenik.[18] Zerovalent palladium complexes were prepared by the procedure of Chatt et al.[19] Cations of the type Pd(diphosphine)$_2^{2+}$ were prepared by the method of Westland.[20]

$[Pd_2(Ph_2PCHCHPPh_2)_2(CNCH_3)_2][PF_6]_2$. *cis*-Bis(diphenylphosphino)ethylene (0.14 g, 3.36 mmol) dissolved in 10 mL of acetonitrile was added to a very pale yellow solution of 0.14 g (0.18 mmol) of $[Pd_2(CNCH_3)_6][PF_6]_2$ in 10 mL of acetonitrile. The intensely yellow solution was heated under reflux for 20 min, and then its volume was reduced to 10 mL on a rotary evaporator. Ethyl ether was added to the solution dropwise, and the product separated as fine yellow crystals, yield 0.20 g (80%). The product was purified by dissolving it in dichloromethane, filtering the resulting solution, and crystallizing the salt by the addition of ethyl ether. After the product had been isolated through filtration, it was vacuum-dried. Anal. Calcd for $C_{56}H_{50}F_{12}N_2P_6Pd_2$: C, 48.75; H, 3.80; N, 2.02; P, 13.47. Found: C, 48.65; H, 3.75; N, 2.02; P, 12.98.

$[Pd_2(Ph_2P(CH_2)_2PPh_2)_2(CNCH_3)_2][PF_6]_2$. The compound was prepared by the preceding method and obtained as deep yellow plates. Anal. Calcd for $C_{56}H_{54}F_{12}N_2P_6Pd_2$: C, 48.68; H, 3.94. Found: C, 48.81; H, 4.01.

$[Pd_2(Ph_2P(CH_2)_3PPh_2)_2(CNCH_3)_2][PF_6]_2$. This yellow complex was obtained as described above except that 10 mL of ethyl alcohol was added to the acetonitrile solution of the mixed reagents before the solution's volume was reduced to 10 mL. Anal. Calcd for $C_{58}H_{58}F_{12}N_2P_6Pd_2$: C, 49.42; H, 4.15. Found: C, 49.18; H, 4.07.

$[Pd_2(Ph_2P(CH_2)_4PPh_2)_2(CNCH_3)_2][PF_6]_2$. This material was prepared via the method used for the first example except that, after mixing and refluxing of the initial reagents, the yellow solution was taken to dryness on a rotary evaporator. Dichloromethane was added in just sufficient quantity to dissolve the deep yellow oil. Upon the addition of ethyl ether, the product formed yellow crystals. Anal. Calcd for $C_{60}H_{62}F_{12}N_2P_6Pd_2$: C, 50.12; H, 4.35. Found: C, 50.42; H, 4.31.

$[Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2][PF_6]_2$. This salt was obtained by the procedure used for $[Pd_2(Ph_2P(CH_2)_4PPh_2)_2(CNCH_3)_2][PF_6]_2$. Anal. Calcd for $C_{68}H_{66}F_{12}N_2P_8Pd_2$: C, 51.97; H, 4.23. Found: C, 51.87; H, 4.31.

Physical Measurements. Infrared spectra were recorded from Nujol mulls on a Perkin-Elmer 180 infrared spectrometer. Electrical conductivities were determined by use of an Industrial Instruments conductivity bridge with 10^{-3} M acetonitrile solutions. ^1H NMR and proton-decoupled ^{31}P NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer at 200 and 81 MHz, respectively. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra and the high-frequency-positive convention, recommended by IUPAC, has been used in reporting chemical shifts.

Simulations of the entire ^{31}P spectra were performed by using the noniterative simulation routine of the Nicolet software on a Model 1180 Nicolet data system. This simulation routine is a modified version of LAOCOON III. The fit of the simulation was based on matching of the individual peak positions and intensities of the observed and the calculated spectra.

Results

Conproportionation Reactions. The reaction of bis(benzonitrile)palladium dichloride, tris(dibenzylideneacetone)dipalladium, and bis(diphenylphosphino)methane (dpm) in dichloromethane for 0.5 h at 38 °C yields **2** in 80% yield. Under similar conditions with use of $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3) or *cis*-$Ph_2PCHCHPPh_2$ as the diphosphine, brown solids are obtained. Analysis of these materials by ^{31}P NMR spectroscopy shows that they are mixtures with the principal component being (diphosphine)$PdCl_2$. Separation and identification of the other components of these mixtures have not proven to be feasible, and so other routes to diphosphine complexes of Pd(I) were sought.

The $^{31}P\{^1H\}$ spectra of the various palladium(II) complexes are reported in Table I. The unusual ^{31}P chemical shift for $Pd(dpm)Cl_2$ is noteworthy. In most cases coordination of a tertiary phosphine to a metal causes shifts of the ^{31}P resonance of the complexed phosphine to higher frequency. This deshielding occurs for monodentate phosphine and for bidentate phosphines which form chelate rings of various sizes. The

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Table I. Phosphorus and Proton Nuclear Magnetic Resonance Parameters for Palladium Compounds

compd	δ	
	$^{31}P\{H\}$ NMR[a]	$^{1}H(CH_2)$ NMR[a]
$Ph_2AsCH_2AsPh_2$		2.6
$Ph_2PCH_2PPh_2$	−21.6	2.8 (t, $^2J_{PH}$ = 1.5 Hz)
$Ph_2P(CH_2)_2PPh_2$	−11.6	2.1 (m)
$Ph_2P(CH_2)_3PPh_2$	−16.7	
$Ph_2P(CH_2)_4PPh_2$	−15.3	
$Ph_2PCHCHPPh_2$	−23.3	
$Ph_2P(CH_2)_2PPh(CH_2)_2Ph_2$	−11.9, −15.7 (2:1, $^3J_{PP}$ = 29.1 Hz)	
$Pd(Ph_2PCH_2PPh_2)_2$	22.6[b]	
$Pd_2(Ph_2PCH_2PPh_2)_3$	14.5[b]	3.0 (br)
$Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$	−2.5	4.17 (quintet, J_{PH} = 4 Hz)
$Pd(Ph_2PCH_2PPh_2)Cl_2$	−53.7	4.28 (t, J_{PH} = 10.7 Hz)
$Pd(Ph_2P(CH_2)_2PPh_2)_2$	31.4[b]	2.1 (m)[b]
$Pd(Ph_2P(CH_2)_2PPh_2)Cl_2$	64.2	2.4 (d, J = 22.8 Hz)[d]
$Pd(Ph_2P(CH_2)_2PPh_2)_2Cl_2$	56.5	
$Pd(Ph_2P(CH_2)_3PPh_2)Cl_2$	11.9	2.6–1.8 (m)
$Pd_2(Ph_2AsCH_2AsPh_2)_2Cl_2$		3.9
$[Pd(Ph_2P(CH_2)_2PPh_2)_2][PF_6]_2$	58.9[c]	
$Pd_2(dam)(dpm)Cl_2$	−2.47	3.7

[a] In $CDCl_3$ unless otherwise indicated; m indicates multiplet. [b] In C_6D_6. [c] In CD_3CN. [d] Doublet with fine structure on outside wings.

diphosphine in Pd(dpm)Cl_2, however, is more shielded than the free phosphine. We have confirmed that a similar increase in shielding occurs with other halides and pseudohalides. Further study into the origin of this effect is required.

Substitution Reactions of $Ph_2(Ph_2AsCH_2AsPh_2)_2Cl_2$ (3). The behavior of **3** toward phosphines has been monitored by ^1H and ^{31}P NMR spectroscopy. NMR parameters for relevant compounds are compiled in Table I. The concentration of **3** may be conveniently monitored through observation of the methylene singlet of **3** at 3.93 ppm, and loss of the diarsine ligand is readily detected through the growth of the methylene resonance of free bis(diphenylarsino)methane (dam) at 2.60 ppm.

Addition of 1 molar equiv of dpm to **3** produces an ^1H NMR spectrum consisting of resonances due to dam at 2.60, **3** at 3.93, and **2** at 4.14 ppm (quintet, J_{P-H} = 4.0 Hz). No free dpm is present, but a weak peak at <10% the intensity of the peaks due to **2** and **3** is present at 3.70 ppm. This peak is assigned to the methylene protons of the mixed-ligand complex Pd_2(dpm)(dam)Cl_2. The ^{31}P NMR spectrum consists of a singlet at −2.47 ppm due to **2** and a weak singlet at −5.0 ppm which we assign to Pd_2(dpm)(dam)Cl_2. Addition of a second equivalent of dpm to this mixture results in the total loss of the ^1H and ^{31}P features ascribed to Pd_2(dpm)(dam)Cl_2 and the growth of resonances due to **2** and free dam. The introduction of further quantities of dpm causes the growth of the resonance due to free dpm but no change in the intensity of the resonances due to **2** or free dam. However the presence of excess dpm in the mixture does result in broadening of the ^1H NMR resonances of **2** and free dpm so that the spin–spin splitting is no longer resolved. The ^{31}P resonances of **2** and free dpm are also broadened when they are admixed. The line broadening in both ^1H and ^{31}P spectra is attributed to rapid exchange of the phosphine ligand between free and coordinated sites. While the observation of substitution of an arsine ligand by a phosphine ligand in a planar complex is not in itself unusual, the occurrence of substitution in these crowded binuclear complexes is of note. On the presumption that these substitution reactions occur by the associative path which is well established for many planar complexes, the occurrence of facile substitution indicates that rather large molecules like bis(diphenylphosphino)methane have access to the palladium centers in **2** and that, despite the presence of eight phenyl rings about the two directly bound metal ions in **2**, there is little steric protection of these metal ions. The onset of rapid (NMR time scale) ligand exchange between free bis(diphenylphosphino)methane and **2** presents even more striking evidence of the accessibility of the metal centers to incoming nucleophiles.

The products of the addition of bis(diphenylphosphino)ethane to **3** are solvent dependent. In chloroform solution the addition of the diphosphine results in the liberation of the diarsine so that all of the **3** present is consumed by the addition of 2 molar equiv of diphosphine. The ^{31}P spectrum indicates, through the growth of a peak at +64.1 ppm, that the only product formed when 1 equiv of diphosphine was introduced was $Pd(Ph_2PCH_2CH_2PPh_2)Cl_2$. When more than 2 equiv of the diphosphine were added, the growth of a peak at +56.7 ppm indicated that $Pd(Ph_2PCH_2CH_2PPh_2)_2{}^{2+}$ was formed as well. The oxidizing agent for this reaction must be the solvent itself. We suspect that the reaction occurs by disproportionation of the Pd(I) complex via eq 2. The Pd(0) complex is

$$Pd_2(Ph_2AsCH_2AsPh_2)_2Cl_2 + 3Ph_2PCH_2CH_2PPh_2 \rightarrow Pd(Ph_2PCH_2CH_2PPh_2)Cl_2 + 2Ph_2AsCH_2AsPh_2 + Pd(Ph_2PCH_2CH_2PPh_2)_2 \quad (2)$$

then oxidized to $Pd(Ph_2PCH_2CH_2PPh_2)Cl_2$ by the solvent. Oxidation of Pd(0) complexes to the corresponding Pd(II) dichloride is well established for Pd(0) species in chloroform solution. Control experiments using authentic $Pd(Ph_2PCH_2CH_2PPh_2)_2$ demonstrate, in fact, that the required oxidation does occur. In benzene solution the ^{31}P NMR measurements indicate that the product formed by addition of 1 or 2 equiv of the diphosphine is $Pd(Ph_2PCH_2CH_2PPh_2)_2$ (resonance at 31.3 ppm); no free diphosphine or Pd(II) complex is present. Since no oxidized form of the phosphine is detected, we suspect that the diarsine is operating as the reducing agent for this reaction. Despite the difference in the behavior of this system with solvent, one thing is clear: no new Pd(I) complex is formed in this reaction.

Substitution Reactions of $Pd_2(CNCH_3)_6{}^{2+}$ with Diphosphines. Addition of the diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 2–4) and *cis*-$Ph_2PCHCHPPh_2$ to $[Pd_2(CNCH_3)_6][PF_6]_2$ in a 2:1 molar ratio produces deep yellow solutions from which salts of the composition $[Pd_2(\text{diphosphine})_2(CNCH_3)_2][PF_6]_2$ may be readily crystallized. These salts have good solubility in acetone, acetonitrile, and dichloromethane and poor to negligible solubility in ethyl ether, ethyl alcohol, and water. Physical data characterizing these compounds are recorded in Table II. The electrical conductivities of acetonitrile solutions are consistent with their formulation as 1:2 electrolytes. The infrared spectra of all compounds show bands characteristic of terminal isocyanide ligands, the diphosphine ligands, and the hexafluorophosphate anions. No bands indicative of the presence of bridging isocyanide ligands are observed. The ^1H NMR spectra in each case show a sharp singlet due to the isocyanide ligands. Complex multiplets due to the aromatic and methylene group are also observed at the appropriate intensities, but these features are of low information content and are not included in the table.

The ^{31}P NMR spectra are diagnostic of the structure of these cations. In each case the spectra consist of a widely spaced doublet of doublets due to the cation as well as the characteristic septet of the hexafluorophosphate ion centered at −143 ppm (J = 706.2 Hz). The doublet of doublets observed for the cation is consistent with a structure in which each end of the diphosphine ligand is in a chemically distinct

Table II. Physical Properties of Palladium(I) Diphosphine Complexes

compd	Λ_M,[a] Ω^{-1} cm^2 mol^{-1}	ν_{CN},[b] cm^{-1}	^{1}H NMR[c]	^{31}P{H} NMR[a,d]		
			δ(CH$_3$NC)	δ	δ	$^2J_{P-P}$, Hz
$[Pd_2(Ph_2PCH_2CH_2PPh_2)_2(CNCH_3)_2][PF_6]_2$	284	2218	3.47	50.78	38.45	5
$[Pd_2(Ph_2PCHCHPPh_2)_2(CNCH_3)_2][PF_6]_2$	250	2226	3.09	57.01	52.86	10
$[Pd_2(Ph_2P(CH_2)_3PPh_2)_2(CNCH_3)_2][PF_6]_2$	276	2213, 2196	3.19	5.71	−10.77	18
$[Pd_2(PPh_2P(CH_2)_4PPh_2)_2(CNCH_3)_2][PF_6]_2$	280	2209	3.40	25.24	2.48	15.3
$[Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2][PF_6]_2$	314	none	none	41.5[e]		[g]
				27.8[f]	60.4[f]	

[a] In acetonitrile solution. [b] As Nujol mull. [c] In acetonitrile-d_3 solution; in ppm downfield from Me$_4$Si. [d] In ppm with 85% H$_3$PO$_4$ as reference. [e] $\delta(P_a)$. [f] $\delta(P_b)$ or $\delta(P_c)$. [g] $J_{P_a-P_b} = 12$ Hz, $J_{P_a-P_c'} = 10$ Hz, $J_{P_a-P_b'} = 3$ Hz, $J_{P_a-P_c} = 2$ Hz, $J_{P_b-P_b'} = 2$ Hz, $J_{P_b-P_c'} = 330$ Hz, $J_{P_b-P_c} = -9$ Hz, and $J_{P_b-P_c} = 4$ Hz.

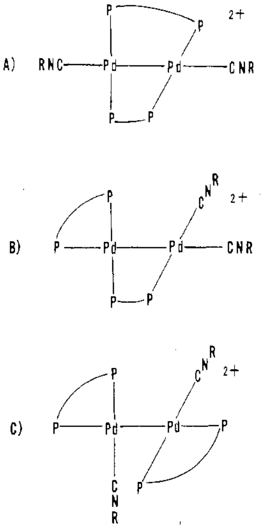

Figure 1. Structures considered for complexes of the type Pd$_2$(diphosphine)$_2$(CNR)$_2{}^{2+}$.

environment. The small (5–18 Hz) coupling constants observed in all cases are indicative of a cis orientation of the two dissimilar phosphorus atoms.

On the basis of the ligand skeletons anticipated for these palladium(I) dimers, the three structures shown in Figure 1 are possible for Pd$_2$(diphosphine)$_2$(CNCH$_3$)$_2{}^{2+}$. Structure A has only a single phosphorus environment and would produce a singlet in the ^{31}P NMR spectrum and a single methyl resonance in the ^{1}H NMR spectrum. Structure B incorporates four phosphorus sites and should display prominent trans P–P splitting in the ^{31}P NMR spectrum as well as two methyl resonances in the ^{1}H NMR spectrum. Structure C contains two distinct types of phosphorus environments and a single type of isocyanide ligand. This structure is wholly and uniquely consistent with all the spectroscopic observations.

These cations show no tendency to insert carbon monoxide or isocyanide into their metal–metal bonds. In this respect their reactivity parallels that of Pd$_2$(CNCH$_3$)$_6{}^{2+}$. However they do show evidence of fluxional behavior since their ^{31}P NMR spectra are temperature dependent. Figure 2 shows the ^{31}P NMR spectrum of [Pd$_2$(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$(CNCH$_3$)$_2$][PF$_6$]$_2$ in acetonitrile solution over the temperature range 24–75 °C. As can be seen, the two barely resolved doublets broaden and eventually merge upon warming. On cooling, these changes are completely reversed. Similar reversible, temperature-dependent line broadening has been observed for Pd(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_2$(CNCH$_3$)$_2{}^{2+}$ (n = 2, 3). Owing, in part, to the greater separation between the doublets in these spectra, coalescence was not achieved by 75 °C in these two cases. The complex where n = 4 was not examined.

The same mechanism proposed to account for the fluxional behavior of Pd$_2$(CNCH$_3$)$_6{}^{2+}$ can account for and anticipates the temperature-dependent ^{31}P NMR spectral observation

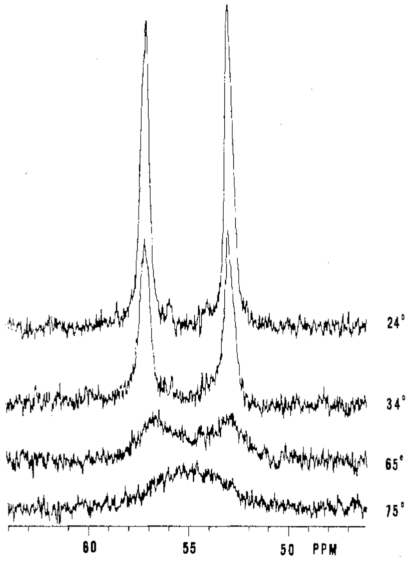

Figure 2. Temperature-dependent ^{31}P{^{1}H} NMR spectrum of [Pd$_2$(Ph$_2$PCH=CHPPh$_2$)$_2$(CNCH$_3$)$_2$][PF$_6$]$_2$ in acetonitrile solution.

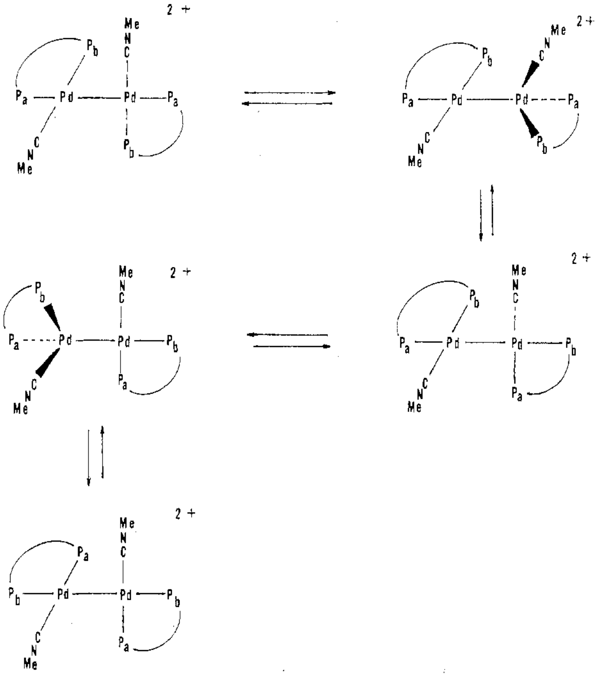

Figure 3. Mechanism for interconversion of phosphorus environments in Pd$_2$(diphosphine)$_2$(CNCH$_3$)$_2{}^{2+}$.

described for Pd$_2$(diphosphine)$_2$(CNCH$_3$)$_2{}^{2+}$. This mechanism as adapted to these diphosphine complexes is shown in Figure 3. Transient polarization of the Pd–Pd bond gives rise to Pd(0)–Pd(II) intermediates (or transition states) in which the

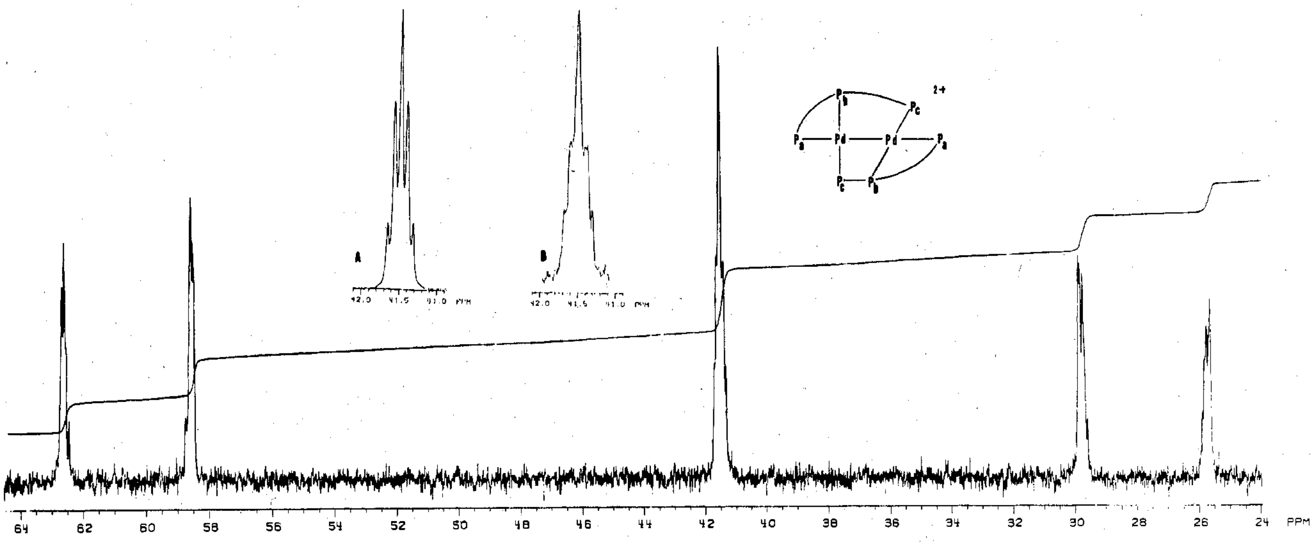

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of $[Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2][PF_6]_2$ in acetonitrile solution at 24 °C. The portion of the spectrum due to PF_6^- is not shown. The multiplet at 41.5 ppm is assigned to P_a, the multiplets between 25 and 30 ppm are due to either P_b or P_c, and the multiplets between 58 and 63 ppm are due to either P_c or P_b. The insert shows an expansion of the multiplet at 41.5 ppm: A, simulated; B, experimental.

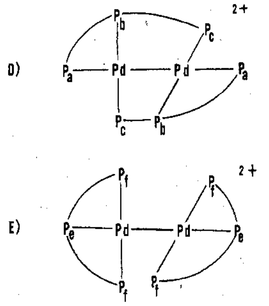

Figure 5. Possible structures for $Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2^{2+}$.

pseudotetrahedral geometry at the Pd(0) center causes the two ends of the phosphine ligand to become equivalent. Reversion to planar geometry at both ends then can interchange the two ends of the diphosphine ligand between the axial and equatorial coordination sites. Such a mechanism is preferable to any involving Pd–P bond breaking since each palladium in these dimers is already an electron-deficient, 16-electron ion.

Substitution of $Pd_2(CNCH_3)_6^{2+}$ with $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$. Addition of the triphosphine $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$ to $[Pd_2(CNCH_3)_6][PF_6]_2$ produces an intensely yellow solution from which $[Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2][PF_6]_2$ may be isolated as yellow crystals. The electrical conductivity of an acetonitrile solution of the complex is consistent with its formulation. The infrared and ^1H NMR spectra of the complex indicate that no isocyanide ligands remain. The ^{31}P NMR spectrum of the complex is shown in Figure 4. For total substitution of all isocyanide ligands of $Pd_2(CNCH_3)_6^{2+}$ by a linear tridentate ligand, two structures are possible as shown in Figure 5. The unbridged structure E contains two types of phosphorus sites and should produce a ^{31}P NMR spectrum grossly similar to that of the free ligand. The actual spectrum is more complex, but entirely consistent with the bridged structure D. At low resolution the spectrum of $[Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2]^{2+}$ consists of a single line at 41.5 ppm due to the axial phosphine a and AB quartet due to the trans, equatorial phosphines b and c. At higher resolution these features show further splitting due to weak cis couplings. The entire spectrum has been fit by a computer simulation. Those spectral parameters are given in Table II. The insert of Figure 4 shows a comparison between the finer details (observed and simulated) of the most intense feature. Similar agreement was found for each of the other features in the spectrum. As expected the trans P_b–P_c coupling is large (330 Hz) while the cis P–P couplings, the three-bond couplings, are much smaller (2–12 Hz). The magnitudes of the cis P–P couplings are consistent with the cis P–P coupling found for $[Pd_2(\text{diphosphine})_2(CNCH_3)_2]^{2+}$. Because of the symmetry of the molecule, the three-bond, trans P_a–P_a coupling cannot be determined from the spectrum.

Discussion

The reaction of polydentate ligands with multinuclear metal complexes can lead to a variety of reactions including substitution, dissociation into smaller fragments with retention of oxidation state,[21] and disproportionation into smaller fragments with different oxidation states.[22] Substitution reactions can occur with retention of the cluster geometry[23] or with its reorganization,[24] particularly of bridge/terminal carbonyls. In the case of reactions of phosphines with $Pd_2(CNCH_3)_6^{2+}$ simple substitution occurs with triphenylphosphine, $Ph_2P(CH_2)_nPPh_2$ (n = 2–4), *cis*-$Ph_2PCH{=}CHPPh_2$, and $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$. Bis(diphenylphosphino)methane departs from this pattern by causing insertion of an isocyanide into the Pd–Pd bond upon reaction.

The coordination positions taken up by polydentate ligands in binuclear and more complex multinuclear species is difficult to predict. Two extreme roles can be clearly identified. Bis(diphenylphosphino)methane is constructed so that the bite and orientation of its lone pairs are more suitable for bridging two metal atoms than for forming a chelate ring about a single metal. In the latter case the four-membered ring that results is clearly strained. Thus this diphosphine acts as a bridging ligand in a wide variety of binuclear complexes[25] and retains that role in polynuclear complexes $Rh_4(CO)_8$-

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[21] For examples see: Bennett, M. A.; Johnson, R. N.; Tomkins, I. B. *J. Am. Chem. Soc.* **1974**, *96*, 61–69. King, R. B.; Kapoor, P. N.; Kapoor, R. N. *Inorg. Chem.* **1971**, *10*, 1841–1850.

[22] For examples see: Laing, M.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1975**, 746. Thornhill, D. J.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2086–2090. Petersen, R. L.; Watters, K. L. *Inorg. Chem.* **1973**, *12*, 3009–3011.

[23] For examples see: Roberts, P. J.; Trotter, J. *J. Chem. Soc. A* **1971**, 1479–1482.

[24] For example see: Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4422–4427.

[25] For a listing of relevant structural data see: Olmstead, M. M.; Lindsay, C. H.; Benner, L. S.; Balch, A. L. *J. Organomet. Chem.* **1979**, *179*, 289–300.

$(Ph_2PCH_2PPh_2)_2$[26] and $Ru_3(CO)_{10}(Ph_2PCH_2PPh_2)$[27] as well. At the other extreme, long-chain diphosphines $R_2P(CH_2)_nPR_2$ ($n > 6$) with bulky substituents on phosphorus form binuclear, macrocyclic metal complexes with trans phosphine ligands on each metal and very long separations between the metals.[28] In these molecules the long span between the metals precludes metal–metal bonding. For intermediate-length diphosphines not only is the stability of bridge vs. chelate structure difficult to estimate, but there is little well-established structural information available. For metal–metal-bonded systems complexes of the type $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$(diphosphine), where diphosphine may be $Ph_2P(CH_2)_nPPh_2$ (n = 2–4) or *cis*-$Ph_2PCH{=}CHPPh_2$, diphosphine-bridged structures exist.[29] Bis(diphenylphosphino)ethane acts as a bridging ligand in $Re_2(Ph_2PCH_2CH_2PPh_2)_2Cl_4$[30] and may behave similarly in $Mo_2(Ph_2PCH_2CH_2PPh_2)_2Cl_4$.[31] For systems which do not contain metal–metal bonds, diphosphine-bridged compounds of d^8 metal ions are known for the two diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 3, 4).[32,33]

For the triphosphine ligand, adoption of the chelating and bridging structure of Figure 5 is not surprising. Meek and co-workers have noted that, for this triphosphine to coordinate all three phosphorus atoms to a single metal atom, the constraints of the bridging methylene groups would limit the trans P–M–P angle (involving the terminal phosphino groups) to no greater than 166°.[34] In the case of the bridging structure this constraint is eliminated. Since there is, presumably, no great barrier to rotation about the Pd–Pd bond, the dihedral angle between the P–Pd–Pd–P group is free to adopt a strain-free orientation. Inspection of space-filling Corey–Pauling–Koltum molecular models indicates that structure D is strain free. A similar geometry for this triphosphine ligand has been proposed for the rhodium polymer $[Rh_4(\text{triphosphine})_3Cl_4]_n$.[34]

Acknowledgment. We thank the UCD NMR Facility and the National Science Foundation for support and Matthey-Bishop for a loan of palladium salts.

Registry No. $[Pd_2(Ph_2PCH_2CH_2PPh_2)_2(CNCH_3)_2][PF_6]_2$, 74525-04-5; $[Pd_2(Ph_2PCHCHPPh_2)_2(CNCH_3)_2][PF_6]_2$, 74525-06-7; $[Pd_2(Ph_2P(CH_2)_3PPh_2)_2(CNCH_3)_2][PF_6]_2$, 74525-08-9; $[Pd_2(Ph_2P(CH_2)_4PPh_2)_2(CNCH_3)_2][PF_6]_2$, 74525-10-3; $[Pd_2(Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2)_2][PF_6]_2$, 74562-11-1; $Pd(Ph_2PCH_2PPh_2)_2$, 74525-11-4; $Pd_2(Ph_2PCH_2PPh_2)_3$, 37266-95-8; $Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$, 64345-29-5; $Pd(Ph_2PCH_2PPh_2)Cl_2$, 38425-01-3; $Pd(Ph_2P(CH_2)_2PPh_2)_2$, 31277-98-2; $Pd(Ph_2P(CH_2)_2PPh_2)Cl_2$, 19978-61-1; $Pd(Ph_2P(CH_2)_2PPh_2)_2Cl_2$, 57650-14-3; $Pd(Ph_2P(CH_2)_3PPh_2)Cl_2$, 59831-02-6; $Pd_2(Ph_2AsCH_2AsPh_2)_2Cl_2$, 67415-28-5; $[Pd(Ph_2P(CH_2)_2PPh_2)_2][PF_6]_2$, 74525-12-5; $Pd_2(dam)dpm)Cl_2$, 74525-13-6; $[Pd_2(CNCH_3)_6][PF_6]_2$, 56116-48-4; $Ph_2AsCH_2AsPh_2$, 21892-63-7; $Ph_2PCH_2PPh_2$, 2071-20-7; $Ph_2P(CH_2)_2PPh_2$, 1663-45-2; $Ph_2P(CH_2)_3PPh_2$, 6737-42-4; $Ph_2P(CH_2)_4PPh_2$, 7688-25-7; $Ph_2PCHCHPPh_2$, 983-80-2; $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, 23582-02-7.

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Synthesis and Structure of Tris[μ-(ethanethiolato)]-bis[dichloro(dimethyl sulfide)tungsten(III,IV)]. A Mixed Oxidation State Dimeric Tungsten Compound

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and PATRICK VAN ROEY

Received March 20, 1980

The title compound was prepared by the reaction of $WCl_4(Me_2S)_2$ with 2 mole equiv of Me_3SiSEt in CH_2Cl_2 solution. A single-crystal X-ray diffraction study has shown that $(Me_2S)Cl_2W(SEt)_3WCl_2(SMe_2)$ possesses a confacial bioctahedral molecular structure with three symmetrical bridging thiolate ligands. The W–W bond length is 2.505 (1) Å, and an unusually short nonbonded contact (3.054 (6) Å) between two of the bridging sulfur atoms is observed. An ESR signal (g = 2.00) was observed for the solid compound at −183 °C. Crystal data are a = 15.678 (5) Å, b = 15.122 (6) Å, c = 15.751 (5) Å, β = 140.69 (1)°, $P2_1/c$, and Z = 4.

Introduction

The synthesis of polynuclear compounds of tungsten and molybdenum has attracted considerable attention.[1-4] Although there are now several well-demonstrated methods for synthesizing compounds with metal–metal bonds,[5] the synthesis and characterization of dimeric μ-thiolato tungsten clusters have not been previously reported. We have been interested in possible routes to such tungsten clusters involving the stepwise introduction of thiolate groups in lieu of chloride ligands. The subsequent reductive elimination of R_2S_2 which

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